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Development of the Volatile Organic Sampling Train (VOST) for Use in Determining Incinerator Efficiency

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DEVELOPMENT OF THE VOLATILE ORGANIC SAMPLING TRAIN (VOST) FOR USE IN DETERMINING INCINERATOR EFFICIENCY

by

Larry D. Johnson
Industrial Environmental Research Laboratory
Research Triangle Park, NC 27711

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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ABSTRACT

Development of the Volatile Organic Sampling Train (VOST) for Use in Determining Incinerator Efficiency.

Larry D. Johnson, Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

The Resource Conservation and Recovery Act regulations require owners or operators of hazardous waste incinerators to demonstrate that the incinerator can achieve adequate destruction efficiency of certain compounds before a permit is issued. Many of the compounds that are commonly of interest are low molecular weight, volatile species.

This paper will discuss the development, initial evaluation, and field application to incinerators of a new sampling train for volatile organic species. The train developed, the Volatile Organic Sampling Train (VOST), is a simple, portable device employing a combination of Tenax and Tenax/charcoal cartridges as the collection agents. Analysis of the sorption cartridges includes a further concentration step which permits the measurement of stack concentrations as low as 0.1 ng/L.

Key Words

stack sampling, volatile organics, hazardous waste, incineration, destruction efficiency, measurement methods development

Introduction

The development and field application of the volatile organic sampling train (VOST) has been unusual in the high speed at which it has progressed, as well as the difficulty of the task it addresses. The development of the train has generated a high degree of interest in the industrial and contractor sectors, primarily because of its application to incinerator trial burns, but also because it fills a void in the stack sampler's arsenal.

This paper describes the concepts behind the VOST, several stages in the development of the train, and a summary of the current status of the VOST technology.

Background

Although the need for an improved stack sampling procedure for volatile organics has existed for years, the situation only became critical in relation to hazardous waste incineration. A reference document designed to assist in planning or review of sampling and analysis programs for hazardous waste incinerators or related combustors has been produced by EPA (1). That document recommends the Modified Method 5 (MM5) train or Source Assessment Sampling System (SASS) for collection of organics with boiling points greater than 100°C. The sorbent breakthrough characteristics associated with lower boiling organics make the use of these trains inadvisable for quantitative collection of compounds boiling

below 100°C. Early drafts of Reference 1 recommended the use of either plastic sampling bags or glass sample bulbs for collection of these compounds. These recommendations were based on the assumption that at least 1000 ug/g of the material was present in the waste feed, and that the destruction efficiency of interest was 99.99%. In early 1982, an urgent need was identified by EPA R&D engineering programs and the Office of Solid Waste. A number of projects had been identified where volatile principal organic hazardous constituents (POHC) were of interest in waste feed at 100 ug/g concentration, and it was necessary to characterize destruction efficiencies on the order of 99.999%. At such low concentrations of POHC in the stack, glass sampling bulbs are useless, and plastic bags are only effective if combined with a concentration technique. Although it is possible to concentrate organics collected in bags by the use of sorbent tubes or other techniques such as cold trapping, it is not recommended because of the following reason. There are drawbacks, difficulties, and operational pitfalls associated with any sampling technique. When two techniques (such as bag sampling of the source and sorbent sampling of the bag) are applied sequentially, the problems are likely to be compounded.

Since the need for a new sampling approach was apparent, and time was an important factor, a meeting of EPA and contractor scientists and engineers was held in April of 1982 to discuss the problem. As a result of that meeting, the basic concepts and train arrangement for the VOST were agreed upon.

Basic Concepts

The schematic diagram of the VOST is shown in Figure 1. The active elements for collection of volatile organics are the two sorbent cartridges, although some compounds may also be collected in the condensate under certain

circumstances. The first sorbent tube is filled with Tenax porous polymer as the primary collection agent, while the second tube contains Tenax and activated charcoal as an extra precaution against breakthrough of the more volatile materials. The glass sorbent tubes are 10 cm by 1.6 cm and hold 1.6 g of Tenax or 1 g of Tenax + 1 g of charcoal. These tubes were choen because they were the largest of the commercially available ambient air sampling tubes and were compatible with existing desorption equipment. Larger tubes allow larger sample volume before breakthrough occurs. Tubes much larger than those chosen, however, become difficult to heat desorb in an effective manner, and would require a new desorber design.

The VOST operates at 1 L/min while the sorbent tubes are maintained at 20°C or less during sampling. It is important that this temperature be maintained at all times, since higher temperaturs may cause breakthrough of the more volatile organics. Six sets of 20 min (also 20 L) samples are collected over a 2 hr sampling period. The first set is analyzed as a "range finder." If adequate amounts of the material of interest are found, then the other five sets are also analyzed in an identical manner. In some instances only three sets of tubes are analyzed, and the others are retained temporarily as possible backup samples. In the event that the first analysis detects no compound of interest, the remaining five sets are desorbed and recollected onto one Tenax tube. Subsequent analysis of that tube gives an effective detection limit five times as low as the single set analysis.

The analysis procedure used with the VOST consists of heat desorption of the Tenax tubes into a small water vessel, followed by EPA Method 624 analysis of the water trap. EPA Method 624 is a purge and trap procedure

followed by gas chromatography/mass spectrometry. The water trap is included since the Tenax cartridges are often very wet and cause problems if desorbed directly into the gas chromatography column. Several attempts have been made to improve this part of the procedure, but none have succeeded as yet.

For further details concerning operation of the VOST or the associated analysis system, see References 2, 3, and 4.

Initial Laboratory Studies

The first laboratory evaluation of the VOST system was assigned to Midwest Research Institute. A synthetic gas generation system was constructed which was capable of producing gas streams fortified with appropriate levels of test compounds. The compounds chosen for evaluation were vinyl chloride, carbon tetrachloride, trichloroethylene, and chlorobenzene. The concentration levels tested were 0.1, 10, and 100 ug/L. A series of 10 test runs were made. The test matrix included runs at each of the four concentration levels, replicate tests at one level, blanks, and a run where the gas included HCl. The HCl run was included since many incinerator emissions contain this compound. Three trains sampled the gas manifold system during each run. The average results from three trains from the experimental series are summarized in Table 1. The single pair data was derived from analysis of individual pairs of cartridges, one Tenax and one Tenax/charcoal. The combined pairs data results from desorption, recollection, and subsequent analysis of multiple pairs following the procedure described earlier. No combined pairs experiments were carried out at the higher

concentration levels since that mode of operation was designed for low concentrations. The combined pairs data appears to exhibit somewhat less deviation from the desired results, but most of the recoveries fall within ± 50%. It is important to note that the presence of HCl did not produce a significant effect in the recovery levels of the organics tested. Some of the variability in the carbon tetrachloride results is believed to be due to blank variability which was improved for later applications by better cleaning, storage, and handling procedures. Vinyl chloride is quite difficult to handle because of its very low boiling point, and some of the data presented in Reference 3 indicates breakthrough of the compound at higher concentration levels. The major conclusion from the first VOST laboratory study was that the concept was sound and that the train and subsequent analysis procedures were capable of producing the data for which they had been designed. Further details of the laboratory study are presented in References 3 and 4.

Initial Field Application

Immediately upon completion of the laboratory study, Midwest Research Institute was faced with field application of the train as part of an engineering study for EPA's Industrial Environment Research Laboratory - Cincinnati in support of the Office of Solid Waste. The train was repackaged into a more compact and rugged arrangement and taken to the field. Difficulties were encountered on the earliest jobs in this series, primarily from high blanks and field contamination. These were soon brought under control, but certainly made the point that sampling very low concentrations of volatile organics in contaminated surroundings can be very

difficult indeed. Severe contamination was encountered with bag samples as well, and the conclusion is clear that adequate field blanks are just as necessary with bag sampling as with VOST.

During the first series of field tests of the VOST, the equipment was also operated at two different sampling rates, and two different total volumes were collected. The low flow rate operation was designated "Slow VOST" and collected 5 L of gas at 250 mL/min. The stack concentrations obtained by the two methods compared very favorably for carbon tetrachloride, chloroform, and tetrachloroethylene. The results for trichloroethylene were less definitive (4). Comparability of "Slow VOST" and the original VOST operating procedure is important because it shows that breakthrough is generally not occurring and that the equipment may be operated successfully in more than one mode.

Further Evaluation of the VOST

The next major project to utilize the VOST was that of emissions testing for the incinerator ship Vulcanus II. This project is described in References 5 and 6. The VOST used in this project employed the inside-inside cartridge design, and was constructed for Radian Corporation (formerly TRW Corporation), Research Triangle Park (RTP), by Nutech Corp., RTP, NC. The inside-inside (I/I) cartridge differs from the inside-outside (I/O) cartridge in that the ends of the glass tube are drawn down to 4.2 mm (1/4-in.) in order to accommodate gas chromatography ferrules. During the heat desorption phase of the analysis, purge gases travel only through the inside of the I/I cartridge but flow over as well as through the I/O tube.

Prior to application of the VOST to the Vulcanus II project, Radian Corporation (formerly TRW Corporation) carried out a laboratory evaluation not unlike that earlier performed by Midwest Research Institute. A synthetic gas stream was generated, and sampled by the I/I style VOST. The data in Table 2 is derived from the more detailed results given in Reference 5. It may readily be observed that the precision, and probably the accuracy, of this data is improved over that given in Table 1. The two reasons that seem to best explain the improvement are that much had been learned about control of contamination and blanks, and that perhaps the I/I design was inherently more resistant to contamination.

At any rate, the data in Table 2 strongly supports the conclusion of the initial laboratory study, that the VOST concept is sound and will perform as originally intended.

The first known application of the VOST to sampling highly water soluble compounds was carried out by EPA's Industrial Environmental Research Laboratory at RTP. The VOST was used to sample methyl vinyl ketone and tetrahydrofuran emissions from a pilot-scale fluidized-bed combustor. This particular VOST was of the I/O type and was constructed for EPA by Envirodyne Engineers following the Midwest Research Institute design. In theory, highly water soluble compounds are more likely to penetrate the first sorbent cartridge and be found in either the condensate or the second sorbent cartridge. It is necessary to perform spiking and recovery experiments in order to determine whether the compounds of interest may be analyzed by the purge and trap method. In the event they are not, some other method (such as direct injection or high performance liquid chromatography) will be necessary tor analysis of the condensate.

In the project described above, the two compounds of interest were both quantitatively recovered by a slightly modified version of the purge procedure. Longer purge times were used, but total volume was kept the same in order to avoid breakthrough. The two compounds were found primarily on the first sorbent cartridge in spite of their relatively high water solubility. All equipment and procedures appeared to work well even though this was the EPA crew's first experience with it (7).

Current Status

The VOST is now available commercially, and ownership and field experience have become more widely spread. Most of the experience has still been with respect to the more "popular" incineration related compounds such as those listed in Tables 1 and 2. The general consensus from users of the train is that it works well in the field and yields good results when used with adequate care and precautions.

Reference 2 is now available to users of the train and those reviewing incinerator sampling plans.

A validation program for VOST is underway and is being managed by EPA's Environmental Monitoring Systems Laboratory at RTP. Audit gas cylinders have been prepared and are available from the same laboratory. A number of other VOST related research programs are near completion and should provide additional insight into the limitations of the train.

Summary

Laboratory experiments and field experience to date have led to the following conclusions.

1. The VOST concept is sound: the train performs well in the field and yields good results in the hands of careful and experienced operators.

2. Sampling and analysis of low concentrations of organics in the presence of high levels of contamination is very difficult. Strong and well planned quality control is essential.

3. Both the I/O and I/I designs are capable of producing good results if proper precautions are taken.

4. Sampling and analysis of water soluble organics may not be as difficult as feared, but this area stills needs exploration.

It appears that the VOST is a generally useful and flexible piece of equipment which will be valuable for other sources in addition to incinerators.

TABLE 1, VOST Recovery Efficiencies, Initial Studies

	Expected, ng/L	% Recovery: vinyl chloride	carbon tetrachloride	trichlorethylene	
Combined Pairs	0.1	111	176	97	104
	1.0	48	88	108	131
	1.0	146	113	105	115
	1.0*	79	110	105	96
Single Pairs	0.1	79	221	79	95
	1.0	63	47	116	153
	1.0	85	55	115	105
	1.0*	95	40	95	90
	10	142	70	109	106
	100	43	108	132	101

*Included HCl

TABLE 2, VOST Recovery Efficiencies, Further Studies

Compound	Expected Value, ng/L	% Recovery
1, 1 dichlorethane	54	105
	77	90
chloroform	69	147
	118	98
1, 2 dichlorethane	77	95
	80	98
carbon tetrachloride	73	91
	74	70
trichloroethylene	67	99
	96	97
1, 1, 2 trichloroethane	66	78
	94	68
	75	120
tetrachloroethylene	107	105

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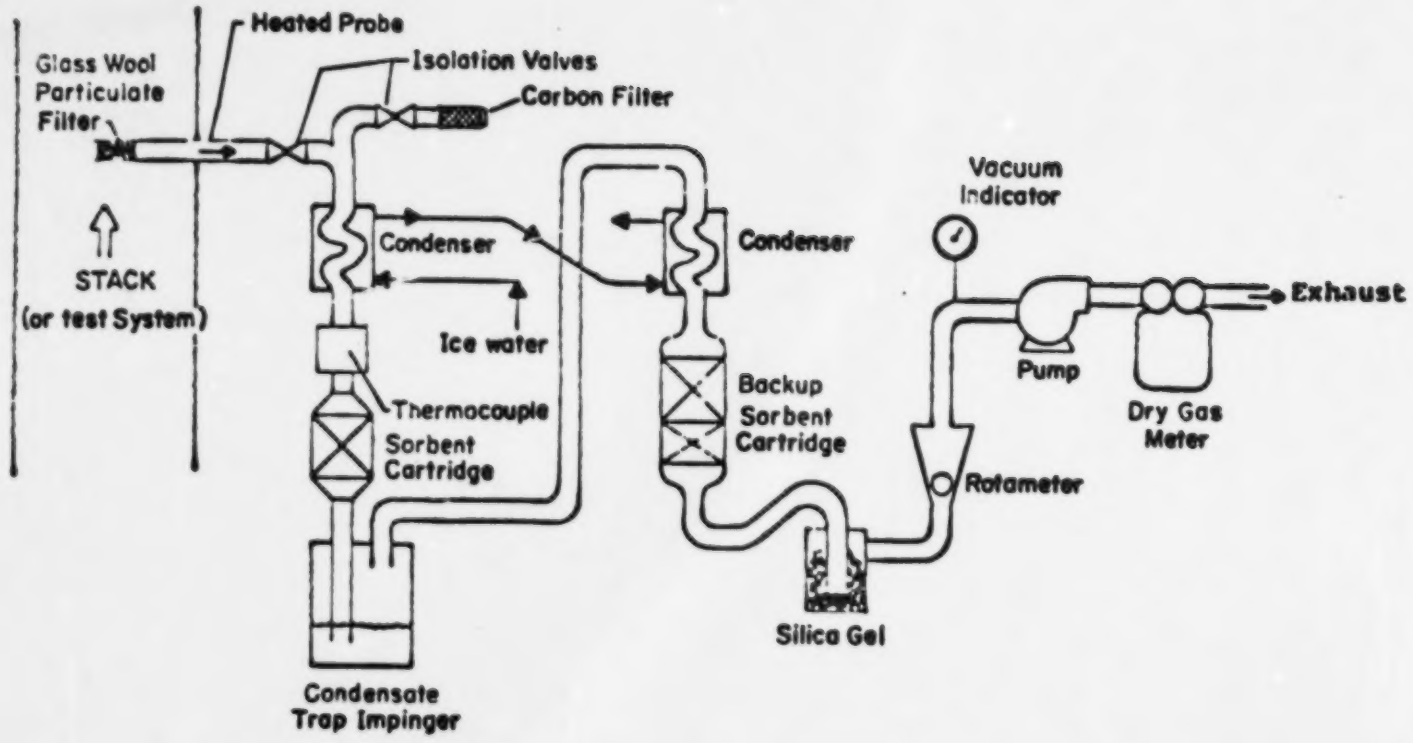

FIGURE 1
SCHEMATIC OF
VOLATILE ORGANIC SAMPLING TRAIN
(VOST)